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DANS LE FLUORURE D'HYDROGENE ANHYDRE

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## USE OF QUINONE SYSTEMS AS ELECTROCHEMICAL pH INDICATORS IN ANHYDROUS HYDROGEN FLUORIDE SOLVENT

### II. POTENTIOMETRIC ACID–BASE TITRATIONS IN ANHYDROUS HF

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#### ABSTRACT

The use of quinone compounds as potentiometric indicators for acidity measurements in anhydrous hydrogen fluoride (AHF) is described. The correct response of such indicators to pF variations and their stability in very acidic media were verified. A comparison is made with the hydrogen electrode which suffers from some drawbacks in AHF; the interest of the quinone acidity indicators is thus pointed out. Acid–base titrations are performed with various acidic and basic solutes and the corresponding titration curves are determined by means of quinonic indicators and a glassy carbon electrode. Values of the basicity constants of the considered solutes are deduced from these titration curves and discussed together with the value ( $10^{-11.5}$ ) of the ionic product of AHF. An acidity scale is established in this solvent: no strong acid appears to exist; even antimony pentafluoride cannot be considered as a strongly acidic compound.

#### INTRODUCTION

It was shown in the first part of this study [1] that, although their behaviour differs from that in aqueous or aprotic media, quinone compounds in anhydrous hydrogen fluoride (AHF) nevertheless exhibit the behaviour of electrochemical systems involving hydrogen ions. Thus the equilibrium potential of solutions of such compounds must be pH-dependent.

Our work previously described was carried out in basic media only (0.1 M KF solution in AHF, or HF + H<sub>2</sub>O mixtures, H<sub>2</sub>O being a base in AHF). The aim of the present paper is to demonstrate that quinone compounds can be used as electrochemical pH-indicators, to follow acid–base titrations, and to set up an acidity scale in AHF.

## EXPERIMENTAL

The apparatus (vacuum line, electrodes, electronics) and the solvent have already been described [1]. All experiments were performed at 0°C.

Apart from potassium fluoroborate (technical grade, Prolabo, Paris), all the chemicals used (acidic or basic solutes, quinones and hydroquinones) were laboratory reagent grade and were kept away from moisture. Potassium fluoride (pro analysi) and antimony pentafluoride (LAB) were Merck-Schuchardt reagents. Tantalum pentafluoride was obtained from Koch-Light. Antimony pentafluoride was handled and the volume delivered was measured with a Teflon syringe (Hamilton, TF 1750 LT) which fitted into a conical hole machined in the lid of a Teflon bottle.

The potentiometric titrations were performed in 100 ml of AHF as follows. Because of the unavoidable presence of small amounts of base in the solvent (traces of water, and KF), the first step was always a titration of a base by an acid until an excess of acid was present. The acidic solution was then back-titrated either by potassium fluoride (strong base) or by a weak base.

The electrochemical indicator was generally a  $10^{-3}$  M mixture of a quinone and the corresponding semiquinone (1,4-naphthoquinone/1,4-naphthosemiquinone or duroquinone/duro-semiquinone) or a mixture of *p*-benzosemiquinone/*p*-hydroquinone. Such mixtures were obtained by partial coulometric reduction of quinone (or oxidation of diphenol) with a glassy carbon electrode. Both constant-current coulometry and constant-potential coulometry were used.

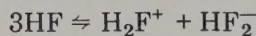
Voltammograms were recorded: (a) before the beginning of the titration; (b) after the titration by an acid; (c) after the back-titration by a base, in order to detect any possible alteration of the electrochemical indicator.

Potentiometric measurements were carried out with a glassy carbon rotating electrode ( $N = 60$  rpm). The reference electrode (Cu/CuF<sub>2</sub>/0.2 M KF) was carefully separated from the bulk of the solution to prevent any alteration of its potential by diffusion of acidic solutes. The Teflon compartment containing the reference electrode was separated from the solution by a porous Teflon sinter and was placed in a larger compartment, containing a weakly basic solution (0.2 M KBF<sub>4</sub>) buffering the possible acidity variations, separated itself from the solution being titrated by another porous Teflon sinter.

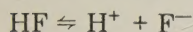
## RESULTS

Before describing the results, we should briefly consider the evaluation of acidity levels in AHF.

Acid-base phenomena in this solvent, the theoretical bases of which are now well known [2,3], are linked to the self-ionization equilibrium, so that we may write:



or more simply:



with:

$$K_i = a_{\text{H}^+} a_{\text{F}^-} \approx [\text{H}^+][\text{F}^-]$$

Thus, acidity may be expressed, either by:  $\text{pH} = -\log a_{\text{H}^+}$ , or by:

$$\text{pF} = -\log a_{\text{F}^-}, \text{ with: } \text{pH} + \text{pF} = \text{p}K_i$$

The acidity scale of AHF is then limited, towards acidic media at  $\text{pH} = 0 (a_{\text{H}^+} = 1 \text{ M})$  and towards basic media at  $\text{pF} = 0 (a_{\text{F}^-} = 1 \text{ M})$ ; an acid-base couple may be placed on this acidity scale, either at the value:

$$\text{pH} = \text{p}K_a$$

with reference to the origin  $\text{pH} = 0$ , or at the value:

$$\text{pF} = \text{p}K_b$$

with reference to the origin  $\text{pF} = 0 (\text{pH} = \text{p}K_i)$ .

If the acidity may be characterized by pF measurements as well as by pH measurements, the choice of either one scale or the other is linked to the possibilities of calibrating the acidity indicating electrode.

Calibration in the pH scale requires a strong acid: owing to the very high acidity level of the solvent, no acidic solute may be considered, beyond doubt, as a strong acid. On the contrary, strong bases like alkali metal fluorides, permit the calibration in the pF scale with a good precision.

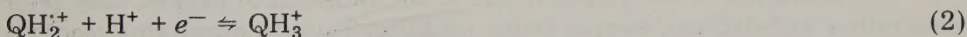
So, in our calculations we referred to pF values, and the acid-base couples constants given are  $\text{p}K_b$  values. In order to calculate  $\text{p}K_a$ , it is necessary to know the corresponding value of  $\text{p}K_i$ .

#### *Variation of the equilibrium potential of quinone/semiquinone systems as a function of pH (or pF)*

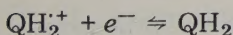
Protonation of quinone compounds was demonstrated in the first part of this work [1] and the following electrochemical processes were postulated:



and



or



The equilibrium potential corresponding to the first system is expressed by:

$$E = E^\circ + 2.3(RT/F) \log [\text{QH}^+][\text{H}^+]/[\text{QH}_3^+]$$

For a mixture of quinone ( $\text{QH}^+$ ) and semiquinone ( $\text{QH}_2^+$ ) of a given composition,

$$E = A - (2.3RT/F) \text{pH} = A' + (2.3RT/F) \text{pF}$$

$A$  and  $A'$  being constants.

The equilibrium potential of such a mixture must be a function of the acidity of the medium and must show a theoretical variation of 54 mV (at  $0^\circ\text{C}$ ) per unit of pH or pF.

A similar result would be obtained for a semiquinone/diphenol mixture, if the electrochemical process were that in the eqn. (2). This is the case when *p*-diphenol is used as an indicator.

Before performing titrations, we verified the potentiometric response of the quinone indicator as a function of the acidity:

(a) *In basic medium.* We followed the variation of the equilibrium potential  $E$  of the quinone electrode in KF solutions (strong base) of increasing concentrations ( $10^{-3}$  M to  $10^{-1}$  M).

The variations of  $E$  vs.  $\log [\text{F}^-]_{\text{added}}$  are approximately linear for fluoride concentrations between  $5 \times 10^{-3}$  M and 0.2 M; the slopes of the corresponding straight lines (0.049 V for 1,4-naphthoquinone/1,4-naphthosemiquinone and 0.054 V for *p*-benzosemiquinone/hydroquinone) confirm the participation of one hydrogen ion per electron in the corresponding electrochemical systems.

It must be noted that we could only plot  $E$  as a function of  $\log [\text{F}^-]_{\text{added}}$  and not of  $\log [\text{F}^-]_{\text{real}}$ : for low fluoride concentrations,  $[\text{F}^-]_{\text{added}}$  may be less than  $[\text{F}^-]_{\text{real}}$  because of the presence of traces of water in the solvent: this may explain the non-linearity of the curves in this zone.

(b) *In acidic medium.* In the same way, we studied the variations of the equilibrium potential as a function of the concentration of acidic solutes.

We first neutralized the residual basic impurities by adding antimony pentafluoride. Further addition of this reagent allowed us to reach acidic media and to obtain the curves representing the variations of the equilibrium potential vs. the logarithm of the concentration of free acid. These curves are nearly straight lines in the concentration range between 0.1 and 1 M and their slopes (0.053 and 0.059 V) confirm the correct response of the quinone electrode. In addition, we observed the evolution of the voltammograms as a function of the acidity. Examples of such voltammograms are shown in Fig. 1, in acidic, strongly basic and weakly basic media respectively. They do not show any alteration of the indicator due to the variation of pH and they remain rather well-defined, even in acidic medium. Thus no interfering reaction of antimony pentafluoride with quinonic indicators seems to occur. Similar results were obtained using  $\text{TaF}_5$  as acidic solute.

From these results, it appears that the two reduction waves of *p*-benzoquinone are shifted in the same manner with variations in pH. On the contrary, for duroquinone and 1,4-naphthoquinone, the second wave ( $\text{Q}(-\text{I})/\text{Q}(-\text{II})$ ) is shifted less than the first one ( $\text{Q}^0/\text{Q}(-\text{I})$ ) as a function of pH. The half-

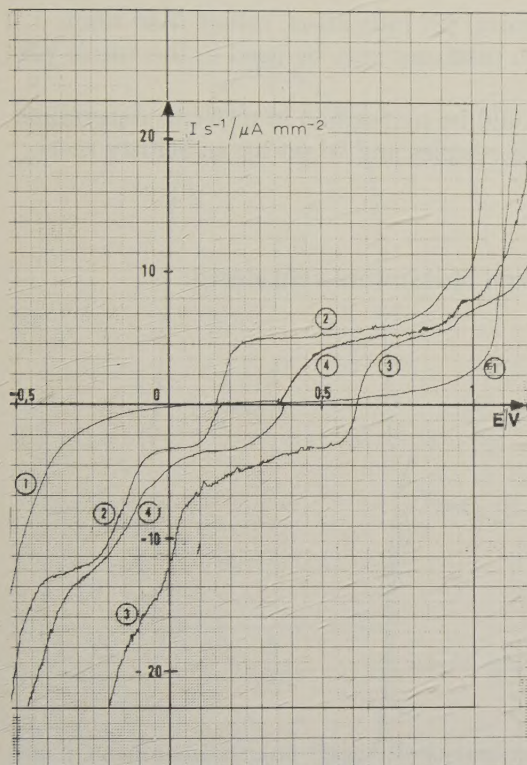
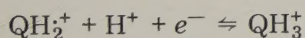
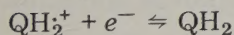


Fig. 1. Use of a mixture of 1,4-naphthoquinone + 1,4-naphthosemiquinone  $10^{-3} M$  as acidity indicator in AHF. Voltammograms obtained at a glassy carbon electrode, at various pH values. (1) Residual current (without quinonic indicator); (2) basic medium (KF); (3) acidic medium ( $[SbF_5] = 0.13 M$ ); (4) weakly basic medium ( $[BF_4^-] = 0.16 M$ ).

wave potential of only the first system varies as  $(2.3RT/F) \text{ pH}$ . This seems to indicate a change in the protonation of the Q(-II) species for these two compounds. In very acidic media, the electrochemical equilibrium would be



In less acidic solutions, it would become



and the half-wave potential would be no longer a function of pH.

This behaviour is shown in Fig. 1; the half-wave potential of the Q(-I)/Q(-II) system shows a notable variation between an acidic solution (3) and a weakly basic one (4) but is very close in the latter case to its value in strongly basic medium (2).

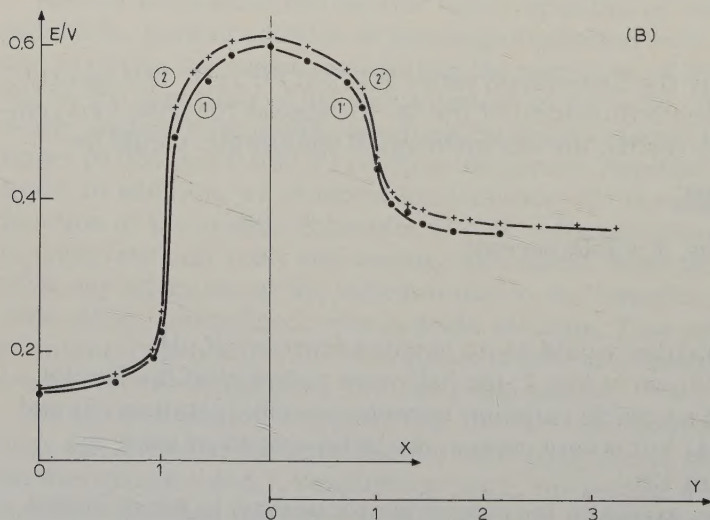
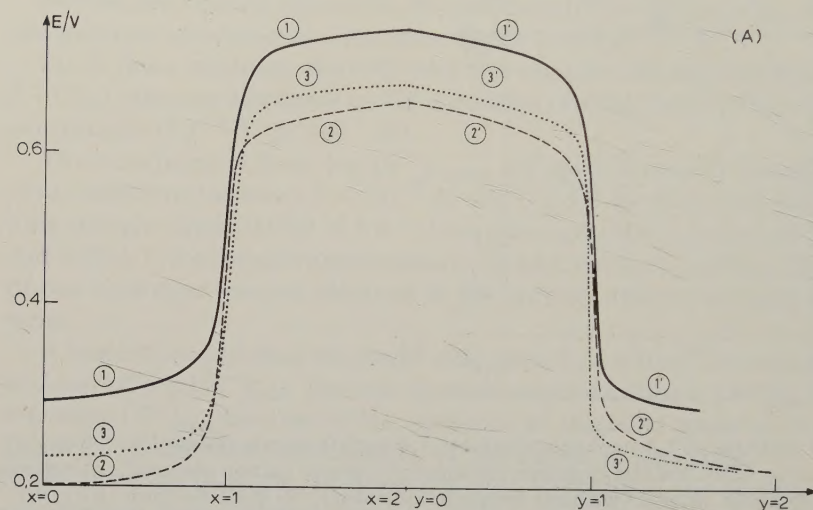
It is thus necessary, except in the case of benzoquinone, to use quinone/

semiquinone mixtures as electrochemical pH indicators, rather than semi-quinone/diphenol mixtures, and such mixtures may be used in the whole pH-range attainable in anhydrous HF.

Then, potentiometric titrations could be performed in order to determine the characteristics of some acid-base couples and to set up an acidity scale.

### *Acid-base titrations*

The following compounds (acids and bases) were considered:



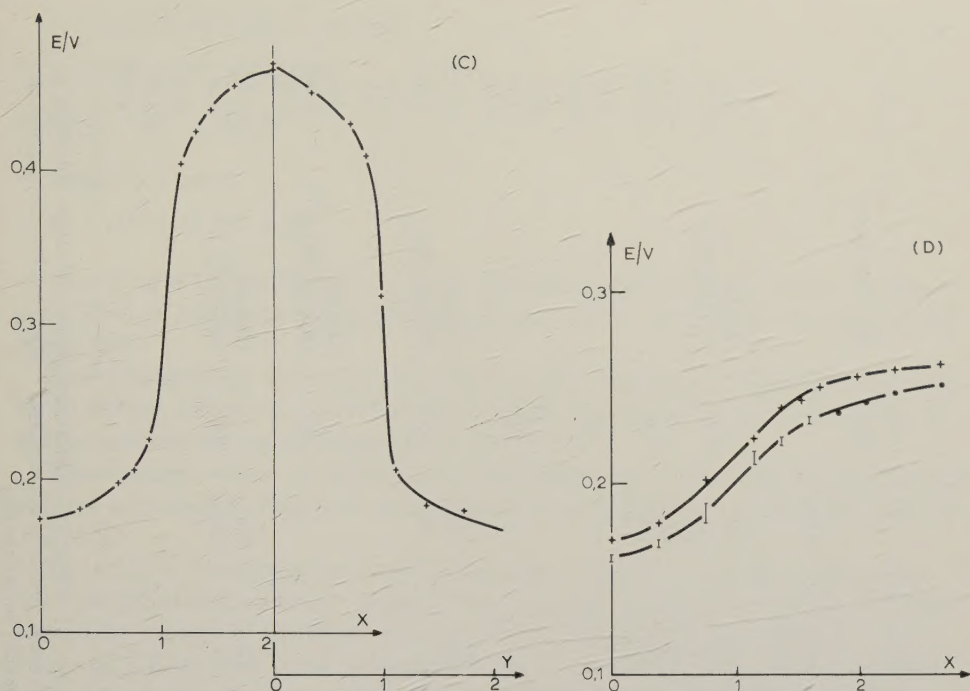
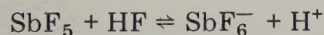
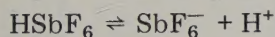


Fig. 2. Potentiometric acid—base titration curves, in AHF, at a glassy carbon electrode, in the presence of quinonic indicators  $10^{-3} M$ . (A): (1), (2), (3) Titrations of a strong base by  $SbF_5$ ; (1'), (2'), (3') titrations of  $SbF_5$  by KF. Indicator: (1'), (1) *para*-benzosemiquinone + hydroquinone; (2), (2') 1,4-naphthoquinone + 1,4-naphthosemiquinone; (3), (3') duroquinone + durosemiquinone. (B): (1), (2) Titrations of a strong base by  $SbF_5$ ; (1'), (2') titrations of  $SbF_5$  by  $KBF_4$ . Indicator: 1,4-naphthoquinone + 1,4-naphthosemiquinone. (C): (1) Titration of a strong base by  $TaF_5$ ; (2) titration of  $TaF_5$  by KF. Indicator: 1,4-naphthoquinone + 1,4-naphthosemiquinone. (D): Titrations of KF by  $HSO_3F$ . Indicator: 1,4-naphthoquinone + 1,4-naphthosemiquinone. X designates the ratio of the amount of acid added to the amount of base being titrated. Y designates the ratio of the amount of base added to the amount of acid being titrated.

antimony pentafluoride: the acidity of  $SbF_5$  is linked with the equilibrium:



or:



tantalum pentafluoride and boron trifluoride exhibit acidic behaviour in the same way (respectively: couples  $TaF_5/TaF_6^-$  and  $BF_3/BF_4^-$ );

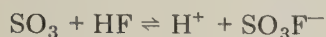
TABLE 1

## Potentiometric titration curves

| Titrated species   | Titrating reagent | Indicator                                 | Slopes <sup>a</sup> /mV |                    | Fig. | pK <sub>b</sub> constants                                   |
|--------------------|-------------------|-------------------------------------------|-------------------------|--------------------|------|-------------------------------------------------------------|
|                    |                   |                                           | before                  | equiv. point after |      |                                                             |
| F <sup>-</sup>     | 0.25 M            | <i>para</i> -benzoquinone<br>Q(-I)/Q(-II) | <i>b</i>                | 53                 | 2A   | Couple<br>SbF <sub>5</sub> /SbF <sub>6</sub> <sup>-</sup>   |
| SbF <sub>5</sub>   | 0.25 M            |                                           | 52                      | 70                 |      | 9.7<br>10.0                                                 |
| F <sup>-</sup>     | 0.24 M            | 1,4-Naphthoquinone<br>Q(0)/Q(-I)          | <i>b</i>                | 52                 | 2A   | 10.03<br>9.48                                               |
| SbF <sub>5</sub>   | 0.26 M            |                                           | 59                      | 87                 |      | 9.8<br>10.0                                                 |
| F <sup>-</sup>     | 0.20 M            | Duroquinone<br>Q(0)/Q(-I)                 |                         |                    | 2A   | 9.3<br>9.0                                                  |
| SbF <sub>5</sub>   | 0.20 M            |                                           |                         |                    |      | 9.37                                                        |
| F <sup>-</sup>     | 0.17 M            | 1,4-Naphthoquinone<br>Q(0)/Q(-I)          |                         |                    | 2B   | 6.27<br>6.36                                                |
| SbF <sub>5</sub>   | 0.20 M            |                                           |                         |                    |      | 6.4<br>6.1                                                  |
| F <sup>-</sup>     | 0.18 M            | 1,4-Naphthoquinone<br>Q(0)/Q(-I)          |                         |                    | 2C   | Couple<br>TaF <sub>5</sub> /TaF <sub>6</sub> <sup>-</sup>   |
| SbF <sub>5</sub>   | 0.16 M            |                                           | <i>b</i>                | 57                 |      | 2.44<br>2.77                                                |
| F <sup>-</sup>     | 0.14 M            | 1,4-Naphthoquinone<br>Q(0)/Q(-I)          | 53                      | 48                 | 2D   | 2.40<br>4.67                                                |
| TaF <sub>5</sub>   | 0.10 M            |                                           |                         |                    |      | 4.8<br>4.2                                                  |
| F <sup>-</sup>     | 0.10 M            | 1,4-Naphthoquinone<br>Q(0)/Q(-I)          |                         |                    | 2B   | 4.8<br>4.19                                                 |
| TaF <sub>5</sub>   | 0.10 M            |                                           |                         |                    |      |                                                             |
| F <sup>-</sup>     | 0.14 M            | 1,4-Naphthoquinone<br>Q(0)/Q(-I)          |                         |                    | 2D   | Couple<br>HSO <sub>3</sub> F/SO <sub>3</sub> F <sup>-</sup> |
| HSO <sub>3</sub> F | 0.21 M            |                                           |                         |                    |      | 2.44<br>2.77                                                |
| F <sup>-</sup>     | 0.14 M            | 1,4-Naphthoquinone<br>Q(0)/Q(-I)          |                         |                    | 2D   | 2.40<br>4.67                                                |
| SbF <sub>5</sub>   | 0.13 M            |                                           | 55 <sup>b</sup>         | 73                 |      | 4.8<br>4.2                                                  |
| SbF <sub>5</sub>   | 0.13 M            | 1,4-Naphthoquinone<br>Q(0)/Q(-I)          | 55 <sup>b</sup>         | 77                 | 2B   | 4.8<br>4.19                                                 |
| SbF <sub>5</sub>   | 0.15 M            |                                           |                         |                    |      |                                                             |
| SbF <sub>5</sub>   | 0.10 M            | Duroquinone<br>Q(0)/Q(-I)                 |                         |                    | 2B   | Couple<br>BF <sub>3</sub> /BF <sub>4</sub> <sup>-</sup>     |
| SbF <sub>5</sub>   | 0.12 M            |                                           |                         |                    |      | 4.2<br>4.8<br>4.19                                          |

<sup>a</sup> Before the equivalence point, the slope indicated is that of  $E$  vs.  $\log(1-x)$ . After the equivalence point, the slope indicated is that of vs.  $\log(x-1)$ .  $x$  represents the fraction of the titrated acidic or basic solute being studied. <sup>b</sup> These values correspond to  $E$  vs.  $\log(1-x)/(1+x)$ , function to be considered if the acid being titrated is not strong.

fluorosulfuric acid is an acid:



water is a base:



The shapes of the titration curves must be same as those of the corresponding kind of curves in aqueous medium and those curves are analyzed in the same way.

The calculations which are reported in more detail elsewhere [4] enabled us to obtain, from the experimental titration curves which appear in Fig. 2, the numerical values summarized in Table 1.

The average values of the basicity constants ( $pK_b$ ) obtained for the various solutes considered, together with their standard deviations, are presented in Table 2.

In order to confirm the correct response of quinonic acidity indicators, we compared some results obtained by using those indicators with those obtained by means of the hydrogen electrode. For that purpose, a titration curve of KF by  $\text{SbF}_5$  was determined by means of the hydrogen electrode, then a back-titration was carried out and followed by potentiometric measurements in the presence of a 1,4-naphthoquinone/1,4-naphthoquinone mixture.

The titration curves (Fig. 3) show the coherence of the two series of measurements as concerns both the position of the equivalence points and the potential (and pH) variations observed. The potential step is of the same order of magnitude in both cases (though a little bit weaker at the hydrogen electrode) but the measurements are much more stable when the quinone electrode is used. It is in fact very difficult to determine precise potential values with the hydrogen electrode, as a fast drift occurs in acidic medium. This is probably due to the deterioration of the finely-divided platinum of the electrode, as can be seen from the aspect of this electrode which is rapidly altered from a normal "velvet black" to a greyish appearance. The com-

TABLE 2

Basicity constants of some acid-base systems in anhydrous hydrogen fluoride

| System         | $\text{SbF}_5/\text{SbF}_6^-$ | $\text{TaF}_5/\text{TaF}_6^-$ | $\text{HSO}_3\text{F}/\text{SO}_3\text{F}^-$ | $\text{BF}_3/\text{BF}_4^-$ | $\text{H}_2\text{O}/\text{H}_3\text{O}^+$    |
|----------------|-------------------------------|-------------------------------|----------------------------------------------|-----------------------------|----------------------------------------------|
| $pK_b$         | 9.63                          | 6.28                          | 2.54                                         | 4.53                        | $\text{H}_2\text{O}$ is nearly a strong base |
| $\sigma(pK_b)$ | 0.36                          | 0.14                          | 0.18                                         | 0.18                        |                                              |

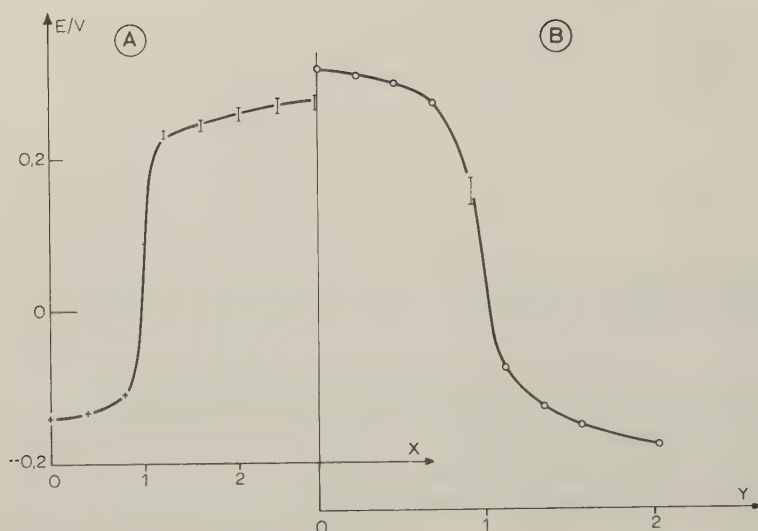


Fig. 3. Comparison of the hydrogen electrode and 1,4-naphthoquinone electrode. (A) Variation of the equilibrium potential of a hydrogen electrode ( $pH_2 = 1$  atm) during the titration of KF by  $SbF_5$ . X designates the titrated fraction of KF: ratio of the amount of acid added to the initial amount of KF. (B) Variation of the equilibrium potential of a glassy carbon electrode in the presence of a mixture 1,4-naphthoquinone + 1,4-naphtho-semiquinone  $10^{-3}$  M during the back-titration of  $SbF_5$  by KF. Y designates the titrated fraction of  $SbF_5$ : ratio of the amount of KF added to the initial amount of acid.

parison between the hydrogen and the quinone electrode demonstrates the correct response of the latter and its advantages for pH measurements in AHF.

## DISCUSSION

The  $pK_b$  values derived from the analysis of the potentiometric titration curves previously described enable us to set up the acidity scale which appears on Fig. 4.

The origin of this scale towards basic media ( $pF = 0$ ) is obtained with alkali metal fluoride solutions (KF or NaF); these compounds turn out, as expected, to be strong bases. Our results on this point agree with researches already published [3,5].

Water also appears to act as a strong base. Neutralizations, by water, of acidic solutions in HF lead to titration curves identical to those obtained when the titrating reagent is a solution of alkali metal fluoride. This fact also is in reasonable agreement with the results of Clifford *et al.* [6] who found nevertheless a slightly positive  $pK_b$  value for water ( $pK_b = 0.26$ ).

Potassium fluoroborate behaves as a weak base in AHF. Boron trifluoride is thus a weak acid ( $pK_b = 4.53$ ).

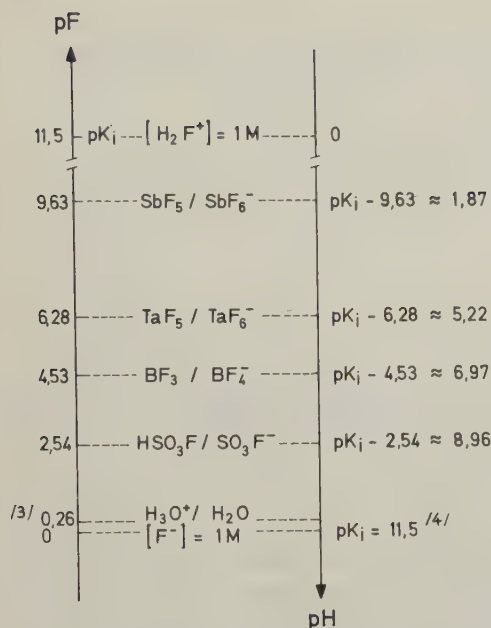


Fig. 4. Acidity scale in AHF (pH and pF).

Fluorosulphuric acid is a very weak acid, and the fluorosulphate ion is a comparatively strong base ( $pK_b = 2.54$ ). This is not surprising, despite the very high acidity level reached by pure  $\text{HSO}_3\text{F}$ , as identical behaviour has already been noted by Gillespie et al. [7] at a similar acidity level in pure sulphuric acid.

Our results are also in agreement with those of Mc Caulay et al. [8] for tantalum pentafluoride which behaves as a weak acid ( $pK_b = 6.28$ ).

There is disagreement about the behaviour of antimony pentafluoride. Some authors [9–11] consider this compound as a strong acid, while others conclude that it is weak [12]. Our mathematical analysis of the titration curves of  $\text{SbF}_5$  by  $\text{KF}$  agrees with the hypothesis of  $\text{SbF}_5$  being a weak acid. Let us point out that, if  $\text{SbF}_5$  was a strong acid, the calibration of the pH-indicating electrode in acidic medium would permit definition of the value  $\text{pH} = 0$ , and thus determination of the self-ionization constant  $K_i$  of the AHF solvent. From our values, we would obtain:

$$pK_i = 10.3 \pm 0.2$$

However, conductimetric measurements [13] led to a value of

$$pK_i = 11.5$$

Considering the characteristics of conductimetric measurements, we must

assume that  $pK_i$  is at least equal to this value. This remark also leads us to conclude that, according to our results, antimony pentafluoride is really a weak acid.

A  $pK_i$  value, close to 11.5, may also be obtained through the comparison of  $pK$  values for the  $BF_3/BF_4^-$  couple. From conductimetric measurements, Kilpatrick and Luborsky [14] evaluated the acidity of boron trifluoride and found  $pK_a = 7.15$ . Our measurements led, for the same couple  $BF_3/BF_4^-$ , to  $pK_b = 4.53$ . Thus we may write:

$$pK_i = pK_a + pK_b = 11.68$$

Thus, the value  $pK_i = 11.5$  approximates the correct value for the ionic product of the solvent.

Using this value, we set up the pH scale represented alongside the experimental pF scale on Fig. 4. This scale extends from  $pH = 0$  ( $[H_2F^+] = 1 M$ , a value that no acid permitted us to reach) to  $pH = 11.5$  ( $[F^-] = 1 M$ ). A neutral solution ( $[H_2F^+] = [F^-]$ ) corresponds to  $pH = 5.75$ , which is approximately the pH value obtained in a buffer mixture of  $TaF_5$  and  $TaF_6^-$  ( $pK_a = 5.22$ ). It appears thus that such a mixture would enable maintenance of the pH in hydrogen fluoride at a value much closer to neutrality than is possible in "pure" solvent. The solvent unavoidably contains traces of water which raise the pH to higher values, because of their strongly basic properties.

The most highly acidic media are the solutions of antimony pentafluoride ( $pK_a = 1.87$ ). Let us point out that, in the comparatively diluted  $SbF_5$  solutions we used (concentrations lower than  $0.25 M$ ) we did not get any evidence of the presence of the polymeric species, like  $Sb_2F_{11}^-$  or  $Sb_nF_{5n+1}^-$  mentioned by Gillepsie [7,15] in mixtures of higher  $SbF_5$  content.

The satisfactory behaviour of potentiometric acidity indicators in AHF even at very high acidity levels, has been demonstrated in this study. The use of such indicators thus allows precise and reproducible pH measurements to be carried out, as it relies on the analysis of potentiometric titration curves. This may prove to be particularly interesting when one considers the difficulties encountered in performing absorptiometric measurements and the problems arising in the interpretation of conductimetric results; hitherto these have been the only methods employed for determining  $pK$  values of acid-base couples in anhydrous hydrogen fluoride.

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